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Densification of Lead Zirconate Titanate Sol-Gel Coatings

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Abstract

A novel method for the densification of sol-gel films is presented. After elimination of organic decomposition products by heat-treatment at 350 ˚C and 450 ˚C, the films are isopressed prior to crystallisation at 550 ˚C. Consequently, porous lead zirconate titanate films, ~0.7 μm in thickness with pore sizes of ~0.1 μm could be transformed into dense 0.2 μm films.

Keywords: Thin Films, Sol-gel preparation, Electroceramics

1. Introduction

Sol-gel deposition is a popular method of producing ferroelectric films such as lead zirconate titanate, PZT. It offers low-capital costs, large-scale coating capability and the potential for good control of chemical composition and homogeneity. Gurkovich and Blum [1] were the first to demonstrate a metal alkoxide approach for preparing bulk gels in this system; the procedures formed the basis for later sol-gel thin film deposition work [2,3]. The majority of thin-film publications on sol-gel PZT yield ~0.1 μm ceramic layers after pyrolysis and crystallisation at temperatures up to ~600 ˚C. This thickness is suitable for applications such as FRAM's where polarisation switching can be achieved at a few volts. However thicker films, up to a

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few microns in thickness are required for other potential applications such as integrated capacitors and microactuators. Unfortunately, coatings from the early sol-gel routes crack when thickness exceeds ~0.1-0.2 μm. The film structure cannot withstand the stresses arising from the gel to ceramic conversion, and any thermal expansion mismatch between the film and substrate. Multiple deposition of ~0.1 μm layers with repetitive heat-treatments can be used to build up layer thickness [4] but it is a lengthy process and increases the total thermal input which can be detrimental to the electrical and mechanical properties of the film and/or component.

Sayer et al. demonstrated that a hybrid particle–gel approach can be applied to produce PZT films a few tens of microns in thickness [5]. Particles are mixed with the sol before spin coating onto a substrate in a technique which has similarities to other slurry-based thick-film methods such as screen-printing or tape-casting. Porosity is a feature of this approach but it has been shown that sol infiltration together with sintering aids can minimise porosity in PZT films ranging from a few micrometers to 50 μm in thickness on platinised silicon substrates [6]; however some porosity remains.

The possibility of increasing the thickness of the standard sol-gel process without adding a particulate component has also been investigated. It has been shown that by moving from the hydrolysis-condensation gelation mechanism involving Ti and Zr isopropoxides, which underpinned the early PZT sol-gel routes, to gelation by molecular bridging using a bi-functional alcohol, 1,3 propanediol, it was possible to produce films with a single-layer, crack-free thickness of ~ 1 μm [7,8]. Later a triol route was developed which could also produce ~1 μm single-layers [9, 10]. The diol route has been demonstrated for multi-layer films up to 10 μm, and the triol route for

films up to 3 μm [11,12], both requiring many fewer repetitions than for sols based on hydrolysis of metal alkoxides. Although surface and fracture sections appeared to be dense by scanning electron microscopy (SEM), subsequently transmission electron microscopy revealed that the films possessed nanoscale porosity, with most pores falling in the range 20-30 nm [10,13].

The addition of polyvinylpyrrolidone (PVP) to standard sols has also been shown to allow the crack-free thickness of PZT to be increased. Layers in the range 0.5–2 μm have been reported [14, 15]. The thicker films contain a high pore fraction, with pore sizes of ~ 100 nm clearly visible in SEM micrographs. Burnout of the high molecular weight PVP is the probable cause of the relatively large pores. Single-layer, crack-free films , 0.7 μm in thickness, have been produced by adding ethylene glycol and ethanolamine to standard sols for the purpose of suppressing crack formation [16]; porosity levels were similar to those of films made with the PVP additive.

The thermal instability of the silicon substrates, which are used because of their technological relevance, precludes the use of high-temperature sintering which otherwise could be used to densify the porous films. Excessive porosity is detrimental in terms of its effect in dissipating piezoelectric strains. However some porosity in the films may be beneficial in terms of providing a toughening mechanism making the coatings more resistant to crack formation during heat-treatments.

This paper demonstrates a novel means of reducing porosity in thick sol-gel films by inserting a pressing step between the pyrolysis and crystallisation heat-treatments. The film selected for this proof-of-principle demonstration is a 0.7 μm single-layer film in which pore sizes are ~ 100 nm, Fig 1.

2. Experimental

The $Pb(Zr_{0.3}Ti_{0.7})$ precursor sols were prepared by dissolving $Pb(OAc)_2 \cdot 3H_2O$ in methanol with gentle warming and stirring for 2h. The $Zr(O^nPr)_4 \cdot {}^nPrOH$ and $Ti(O^nBu)_4$ reagents were mixed together, and an equal volume of acetic acid, and methanol was added to the Zr/Ti solution. The solution was stirred at room temperature for 1h. The Pb solution was added to the Zr/Ti solution and the mixture was further heated under reflux for 2h. After the solution was cooled to room temperature, ethylene glycol (EG) was added in the ratio of 1 ml of EG per 1 g of sol. The concentration of the stock solution was 0.6M. The solution used for coating films was prepared by adding 2 ml of ethanolamine and 2 ml of distilled water to 30 ml of the stock solution. Further details of the synthesis route are presented in reference 16

Films were made by spin-coating the sol onto a $Pt/Ti/SiO_2/Si$ substrate at 1000 rpm for 1 min. The coating was then heated at 350 ºC for 5 min on a hot-plate. For a 'standard' film, crystallisation was carried out at 550 ºC. Films for compaction were heat-treated at 350 ºC and 450 ºC for 5 min prior to isopressing at 200 MPa for 1 min (Stanstead Fluid Power, Stanstead, England); samples were protected by a double layer of latex during pressing. Films were then heat-treated at 550 ºC for 5 min to induce crystallisation.

Polished sections were obtained by gluing two films face-to face and mounting vertically in a resin block; polishing was carried out using a range of abrasives with a final polish using colloidal silica. Microstructures were examined using field emission scanning electron microscopy (LEO Model 1530, Oberkochen, Germany).

3. Results and Discussion

Our new approach to the densification of 'thick' sol-gel films is based on a recognition that the porosity in the final films stems from physical disruption to the films during organic pyrolysis and the elimination of volatile species which occurs during the hot-plate heat-treatment at temperatures of ~ 300-400 ºC. Therefore by physically compacting the porous amorphous film after the pyrolysis stage, in principle it should be possible to produce a dense amorphous structure which can then be heated in the normal manner at ≥ 550 ºC to produce a dense crystalline film. To ensure complete elimination of organics and decomposition of any carbonates, the films were subjected to a second pyrolysis heat-treatment at a slightly higher temperature than normal, 450 ºC. Isopressing was used as the means of compaction but because of the strong bonding between film and substrate, the compaction will be most effective normal to the substrate.

Examination of fracture surfaces can underestimate the amount of porosity in a film, therefore samples were mounted in resin and carefully polished to expose any porosity. The cross-section of such a sample which had been isopressed and at 200 MPa (and crystallised at 550 ºC), Fig 2, clearly reveals the PZT film, the 100 nm Pt electrode layer and the underlying SiO_2/Si substrate; SEM-EDX elemental analysis confirmed this identification. The layer of glue used to bond the films face-to-face has become abraded during polishing and appears as a porous layer between the PZT films in Fig 2.

Compared to the standard film (Fig 1) the PZT film fabricated by the pyrolysis-compaction-crystallisation process is substantially more dense, and much thinner. The 100 nm pores prevalent in the standard film have disappeared and the

film thickness has reduced from ~ 0.7 μm to ~0.2 μm, which is close to the maximum reported thickness of films made by the basic metal alkoxide-acetic acid sol-gel route.

The corresponding surface microstructure is shown in Fig 3; some regions contained a pattern of 10-20 nm wide features; similarly sized features could also be observed running normal to the substrate in cross-sections viewed at higher magnifications, Fig 2b. This form of localised nanoscale cracking may be a form of stress relief in dense films. Indeed surface microstructures of films made by other sol-gel routes, although not exhibiting macroscale cracking, often show a secondary structure of ~ 50 nm wide grain boundaries between more densely packed features [8, 12]; these are likely to be analogous to the fine features displayed in Figs 2b and 3.

In future it will be important to determine the optimum pressing pressures and heat-treatments for producing maximum density films; simple die-pressing akin to that used for laminating tape-cast layers may also be effective. Varying the applied pressures may permit added control of porosity which could be useful for pyroelectric applications where controlled porosity can help increase figures of merit (because of the lower permittivity of porous films) [17].

It will be informative to extend the method to other ‘thick’ PZT film sol-gel routes which are increasingly being reported because of the technological importance of producing films which are a few microns in thickness for micro-transducer and other applications. This would provide a comparison of ‘equivalent dense thickness’ for films made by different routes, and indicate the extent to which differences in reported headline thickness values are simply a consequence of differing levels of porosity.

4. Conclusions

A pyrolysis-compaction-crystallisation procedure has successfully been demonstrated as an effective means of sol-gel film densification. The results provide an indication as to the extent to which a relatively high value of thickness of a single-layer film may simply be a consequence of its high porosity levels. The porosity is caused by physical disruption to the film structure during pyrolysis and the escape of organic decomposition vapours. Sol-gel routes with high contents of organics present after the initial drying stage are prone to such 'bloating' and increase in film thickness. This porosity also inhibits cracking. The pyrolysis-compaction-crystallisation technique will be a valuable tool in formulating an 'equivalent-dense-thickness' scale for evaluating the growing number of sol-gel routes reported to yield single-layer thickness values ≥ 1 μm.

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Figure Captions

1. SEM micrograph of a fractured section of a 0.7 μm film made by the standard sol-gel process involving pyrolysis at 350 ˚C and crystallisation at 550 ˚C

2. SEM micrograph of polished section of a film isopressed and crystallised at 550 ˚C: a) magnification x100,000; b) magnification x150,000.

3. SEM micrograph of top surface of a film isopressed and crystallised at 550 ˚C

Fig 1 SEM micrograph of a fractured section of a 0.7 μm film made by the standard sol-gel process involving pyrolysis at 350 ˚C and crystallisation at 550 ˚C

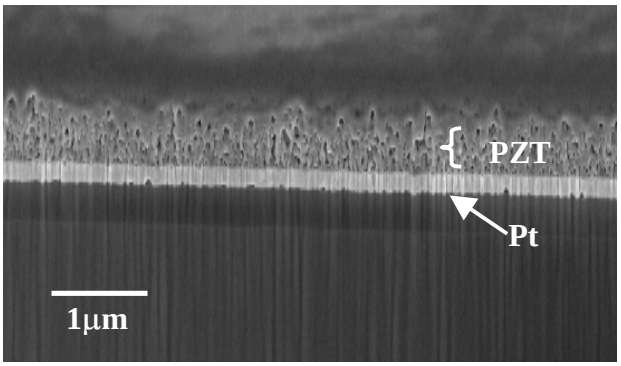

Fig 2 SEM micrograph of polished section of a film isopressed and crystallised at 550 ˚C: a) magnification x100,000; b) magnification x150,000, examples of nanoscale cracks or boundaries are indicated by arrows

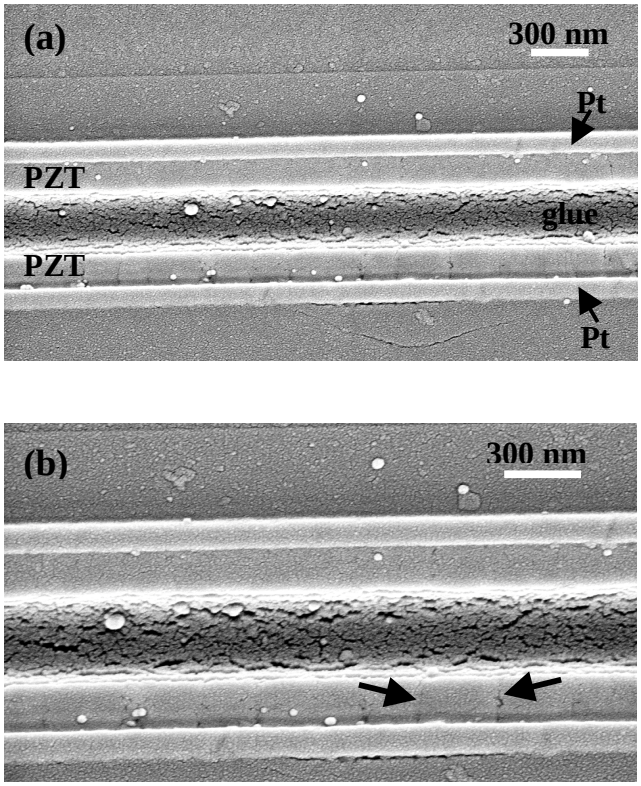

Fig 3 SEM micrograph of top surface of a film isopressed and crystallised at 550 ˚C; examples of nanoscale cracks or boundaries are arrowed.